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HIGH TEMPERATURE TEMPORAL STABILITY OF SELECTED
OXIDIZERS AS SOLIDS AND IN AQUEOUS SOLUTIONS(U) NAVAL
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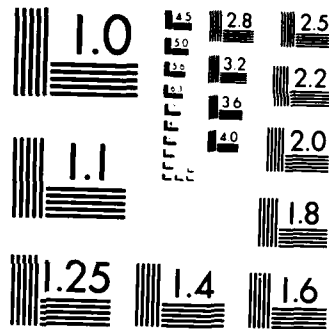
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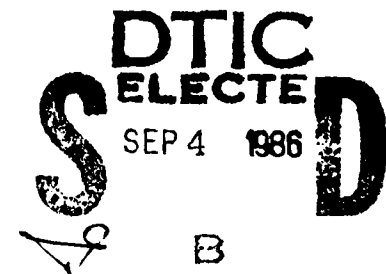
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High Temperature Temporal Stability of Selected Oxidizers as Solids and in Aqueous Solutions

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*Combustion and Fuels Branch
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HIGH TEMPERATURE TEMPORAL STABILITY OF SELECTED OXIDIZERS AS SOLIDS AND IN AQUEOUS SOLUTIONS (U)

INTRODUCTION

Naval elements are potential targets for chemical warfare (CW) or biological warfare (BW), especially during armed hostilities. An effective CW/BW defense posture requires that impacted elements maintain operational status even in a toxic environment. This posture requires the ability to neutralize as necessary CW and/or BW agents on critical surfaces. An element in this decontamination (decon) process is fluids, based on sea or fresh water, which can neutralize agents/toxins.

Most agents/toxins will be oxidized/hydrolyzed by washdown with water containing appropriate additives. These additives include the traditional decontaminant of choice, calcium hypochlorite. Specifically, hypochlorite ion serves to hydrolyze, and oxidize G-agents, a class of CW compounds (Block and Davis, 1978). Furthermore, hypochlorous acid in aqueous solution at pH 7 appears effective in countering BW materials such as spores (Hoffman and Spiner, 1962; Fielding, et al., 1967, 1968; for $\text{HOCl} \rightleftharpoons \text{H}^+ + \text{OCl}^-$, $K = 2.95 \times 10^{-5}$ and $\text{pK} = 7.5$).

In spite of proven effectiveness of hypochlorite for decontamination applications, hypochlorite-based decon presents problems. These problems are in part associated with the chemical nature of hypochlorite. Specifically, in the case of calcium hypochlorite, the solid tends to cake and decompose in storage, and the salt disperses slowly into water, yielding a chalky suspension. Ideally, a decon reagent should be as chemically effective as calcium hypochlorite. Additionally, this ideal reagent should be stable when stored as a solid, be stable in aqueous solution (fresh or sea water) and dissolve rapidly to give a true solution. On-site generation of the ideal decon reagent would also be desirable, to reduce logistics of storing decon reagents.

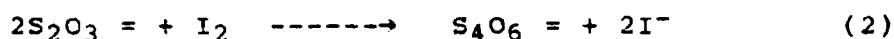
The evaluation process for selecting suitable supplements/replacements for calcium hypochlorite will consider the factors listed above. This report examines the long-term stability at high temperature of selected hypochlorite and peroxide reagents as dry solids, and as aqueous solutions. Such data will help define storage stability of candidate decon reagents, and their stability in decon fluids prepared prior to actual need.

Stability is defined as retention of oxidative capacity with time. For this test, residual oxidative capacity was monitored iodometrically.

EXPERIMENTAL

Candidate oxidizers were examined as dry solids, and as aqueous solutions in distilled water. Multiple aliquots of the reagents (Table 1) were weighed into tared Pyrex petri dishes and placed in an oven set to maintain 80° C. At various times, one solid aliquot of each of the candidates was removed from the oven. The solids were placed in 100 mL of distilled water to yield approximately 0.01 N solutions, which were assayed iodometrically (see below). Aliquots of solid retained at room temperature served as controls in this sequence. Aqueous solutions of the candidate oxidizers were prepared in distilled water, giving 200 mL of approximately 0.01N solution. These solutions were placed in 250 mL round-bottomed flasks, and fitted to a Soxhlet extraction apparatus set to maintain the fluids at 60° C. The condensers of the Soxhlet apparatus were used to minimize solution concentration changes caused by evaporation. At various times, 2.0 mL aliquots of these hot, stored solutions were taken. The oxidizer content of these aliquots was measured iodometrically.

Iodometric titration was used to monitor the oxidizer content of all samples tested. These samples consisted of 2.0 mL aliquots of solution made from dry, heat stressed solid oxidizer, or 2.0 mL aliquots of heat stressed aqueous solution. The following equations describe the iodometric reactions:



Essentially, an oxidizer [hypochlorite ion in (1) above] oxidizes iodide to iodine, which then oxidizes thiosulfate ion. The amount of thiosulfate consumed (added as a standardized solution) corresponds to the amount of oxidizer present in the original aliquot. For the titrations, 2 mL aliquots of the various test solutions (from the stored solid, or stored solution) were added to 50 mL distilled water. The pH of each solution was then adjusted to 4.5 ± 0.5 with 2 drops of 2 N sulfuric acid in distilled water. To the acidified solution were added 2.0 mL of 10% wt./wt. potassium iodide in distilled water. This addition yielded gold color solutions if there was oxidizer in the test aliquot. The kinetics of the reaction between oxidizer and iodide are crucial in this titration. The chlorine based oxidizer reacted essentially instantaneously with added potassium iodide, so that the titration could proceed as described below. However, the peroxygen reagents reacted much more slowly with added iodide. Therefore these test solutions

were allowed to stand prior to titration with standard thiosulfate solution. These standing times are cited in Table 4, and were selected to allow the oxidizer-iodide interactions to proceed, but not necessarily to completion. In some cases (e.g. peroxydisulfate ion), reaction to completion would take so long that one would begin to lose gaseous iodine from the titration vessel upon standing; in these cases, a long, but not infinite reaction time was chosen. (Pellenbarg, 1985, addresses the reaction kinetics between iodide and peroxygen species in more detail). After reaction between iodide and oxidizer, the magnetically stirred solutions were titrated with 0.0375 N sodium thiosulfate solution (Fisher) dispensed from a 10 mL burette, to give a pale yellow color. Two to several drops of soluble starch solution (1.0 g. soluble starch [titrated to a paste with cold water] added slowly with stirring to 100 mL boiling distilled water containing 1 g boric acid [Fisher] as a preservative, cooled and stored in a brown glass bottle) were added to the titration mix to give a dark blue color. Additional thiosulfate solution was added until a clear, colorless endpoint resulted. The total volumes (titer) of thiosulfate solution used to neutralize oxidizer liberated iodine was recorded, and served as a monitor of residual oxidizer in a given sample as a function of time: the more oxidizer present in a given sample, the more thiosulfate solution consumed.

RESULTS AND DISCUSSIONS

Oxidizers as Solids

At 80° C, PACE, a chlorine based oxidizer, exhibited excellent long term stability as a solid, retaining almost 100% of initial oxidizer content after 24 days. The other chlorine containing materials were much less stable as heat-stressed solids. Lithium hypochlorite lost all its oxidizer capacity after only 3 days, and the oxidizer content of calcium hypochlorite fell by approximately two-thirds after 10 days. (Figures 1 - 3)

The peroxygen reagents exhibited mixed stability, compared to the chlorine bearing materials. Sodium perborate and peroxydisulfate were fairly stable with time at 80° C, losing some 50% of initial oxidizer content in 24 days. Conversely, H-48 and sodium percarbonate were markedly unstable as solids at 80° C, and became essentially inactive after only 3 days. (Figures 4 -7).

The solids analyzed above required dissolution prior to measurement of initial or residual oxidizer content. This dissolution process yielded several significant observations. PACE dissolved almost instantly, and gave a no-residue solution at all times in the test sequence. However, the hypochlorite salts, especially after aging at 80° C, dissolved slowly, and

left undissolved precipitates/sediments. These suspended/sedimented solids could prove troublesome when dispersing any decon solution containing a hypochlorite salt; such problems, as clogging of application equipment, should be investigated in more detail.

Like PACE, heat-stressed H-48 and sodium percarbonate solids dissolved rapidly and cleanly, but gave solutions with little residual oxidizer content. The sodium perborate and sodium peroxydisulfate solids tended to dissolve well, and gave solution with fair residual oxidizer content. These latter solutions though, reacted slowly with added iodide, indicating the possibility of a different reaction mechanism between oxidizer and substrate (iodide ion) for the chlorine-based, and some oxygen-based oxidizers. This possible kinetic difference should be examined in more detail to indicate potential new approaches to decon chemistry.

Oxidizers as Solutions

One CW/BW defense scenario could involve the preparation and storage of a decon fluid prior to actual need, so that decon materials would be on hand and ready for use as necessary. Any candidate which rapidly decomposes in solution may prove less than useful in such a field setting. With this possibility in mind, 60° C solutions of candidate oxidizers in distilled water were monitored with time.

At 60° C in solution, PACE decomposed markedly in a few hours, and lost most of its oxidizer capacity in less than one day. Upon prolonged storage of the aged PACE solutions, the initially clear solution yielded yellowish particles as a precipitate. These particulates could cause problems with solution dispensing. In solution, both hypochlorite salts were more stable with time than was the PACE, and indeed, were more stable for a longer time than were the dry, heat-stress solids (Figures 1 - 3). It would be useful to examine mechanisms which could account for the differing stabilities observed in this testing sequence.

The tested peroxygen salts exhibited variable stability in solution, but all decomposed within about 4 days at 60° C (Figures 5 - 8). Thus, sodium perborate retained approximately 60% of its initial oxidizer content after 4 days, while the other candidates were essentially gone in this time. In solution, sodium percarbonate gave a precipitate/sediment, sodium perborate yielded long crystalline needles, while the sodium peroxydisulfate did not change appreciably. The changes in the chemical/physical characteristics of the candidate solutions have implications as to the solutions' ultimate utility as a decon fluid.

CONCLUSIONS

The study described in this report examined the stability in storage at high temperature of seven candidate decon materials tested as dry powders and as aqueous solutions in distilled water. As solids, only PACE, of the chlorine-based oxidizers, exhibited oxidizer capacity for more than 24 hours. Both lithium and calcium hypochlorites decomposed rapidly at high temperatures when stored as solids. The inorganic peroxygen materials sodium perborate and sodium peroxydisulfate were stable as solids at high temperature, while solid H-48 and solid sodium percarbonate lost all oxidizer capacity in approximately 72 hours.

In solution, however, PACE was much less stable than the other chlorine-based oxidizers, and decomposed markedly in less than 24 hours. However, even the lithium and calcium hypochlorites decomposed appreciably in 36 - 48 hours. The peroxygen compounds in solution also exhibited variable, but short lifetimes, with sodium perborate losing only about half its oxidizing capacity after 4 days. The other peroxygen materials were less stable with time in solution. These observations indicate that, in general, the oxidizers studied exhibit instability at high temperatures whether in solution, or as the solid. This fact dictates appropriate logistics when storing solid materials to be added to decontamination fluids, and suggests caution with regard to the use of hot solutions of decon reagents stored for more than a few hours prior to use.

RECOMMENDATIONS

This study has identified several topics which impact directly on the preparation of decon fluids from solid, stored precursors. Specifically needed now are data which:

1. Compare the decon efficiency of the better candidates examined in the study against appropriate CW and BW simulants, and ultimately, against live agents and toxins.
2. Study effective packaging/storage procedures for those candidates which prove effective in decon tests with simulants/agents.
3. Examine the effects of various additives to the oxidizer solutions studied with regards to the residual oxidizer capacity. AFFF is a potential additive in this context, because of its useful surfactant properties and its availability aboard Navy ships.
4. Investigate the degradation of Navy materials (including composites, rubber, etc.) in contact with solutions of the candidates in fresh and salt water, with and without additives such as AFFF.

ACKNOWLEDGEMENTS

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4. Hoffman, R. K., and Spiner, D. R., "Decontamination Procedures for Personnel Handling Biological Weapons," TM12 (AD285543), U.S. Army Biological Laboratories, Ft. Detrick, MD, Sept. 1962.
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TABLE 1: OXIDIZERS TESTED

Name:	Formula Weight	Salt, grams/liter (Normality)
Lithium Hypochlorite *(Lithco)	58.4	6.56 (0.03)
Calcium Hypochlorite (Fisher)	141.1	3.58 (0.025)
Sodium Dichloroisocyanurate (PACE) (Olin)	255.0	6.41 (0.025)
Sodium Perborate (Alfa)	153.8	1.55 (0.01)
Sodium Peroxydisulfate (Alfa)	238.0	2.37 (0.01)
Magnesium Bis (2-Carboxylato mono peroxybenzoic acid) hexahydrate (H-43) (Interox)	496.3	4.96 (0.01)

* Sources

Lithco: Lithium Corporation of America, Bessemer City, NC:
Lithco product is approximately 30% lithium hypochlorite.

Fisher: Fisher Scientific Company, Fairlawn, NJ

Olin: Olin Chemicals, Stamford, CT

Alfa: Alfa Products, Danvers, MA

Interox: Interox America, Houston, TX

TABLE 2: HYPOCHLORITE TEST RESULTS

LITHIUM HYPOCHLORITE

Solids*		Solutions**	
Time (days)	Titer (mL.)	Time (days)	Titer (mL.)
0	2.53	0	2.53
1	0.01	1/8	2.52
3	0.04	1	2.56
10	0.01	6	0.99
18	0.003	8	1.01

CALCIUM HYPOCHLORITE

0	2.93	0	2.93
3	2.21	1/8	2.69
10	0.66	1	2.52
14	0.96	2	2.34
18	1.14	6	1.04
24	0.55	8	1.24

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0	4.30	0	4.77
3	4.22	1/8	3.89
10	3.60	1	0.23
14	3.80	2	0.04
18	4.70	6	0.00
24	4.18	8	0.00

* Solids stored as dry material at 80° C.

** Solutions: Candidates dissolved in distilled water, retained at 60° C.

TABLE 3: PEROXYGEN TEST RESULTS

SODIUM PERBORATE

Solids*		Solutions**	
Time (days)	Titer (mL.)	Time (days)	Titer (mL.)
0	0.44	0	0.33
1	0.36	1	0.24
3	0.31	4	0.18
10	0.38		
14	0.42		
18	0.24		
24	0.22		

SODIUM PEROXYDISULFATE

0	0.18	0	0.18
3	0.21	1	0.07
10	0.14	4	0.05
14	0.22		
18	0.17		
24	0.11		

H-48

0	1.34	0	1.34
3	0.04	1	0.18
10	0.06	4	0.00
14	0.00	8	0.00
18	0.00		
24	0.00		

SODIUM PERCARBONATE

0	0.83	0	0.83
3	0.05	1	0.20
10	0.01	4	0.10
14	0.04		
18	0.00		
24	0.02		

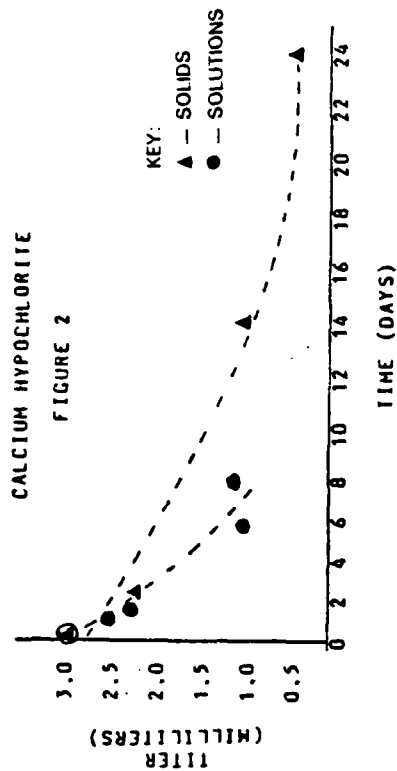
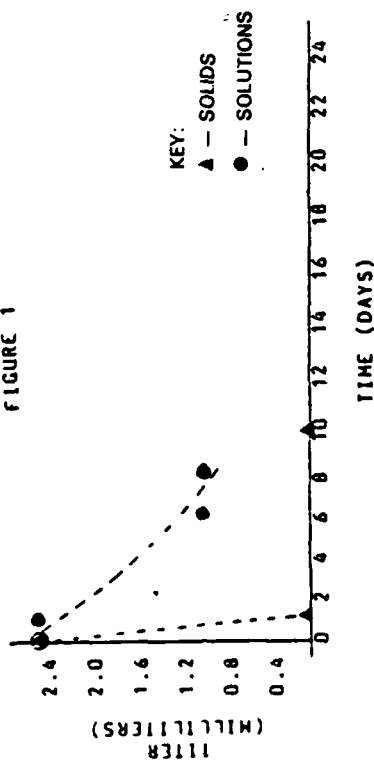
* Solids stored as dry materials at 80° C.

** Solutions: Candidates dissolved in distilled water, retained at 60° C.

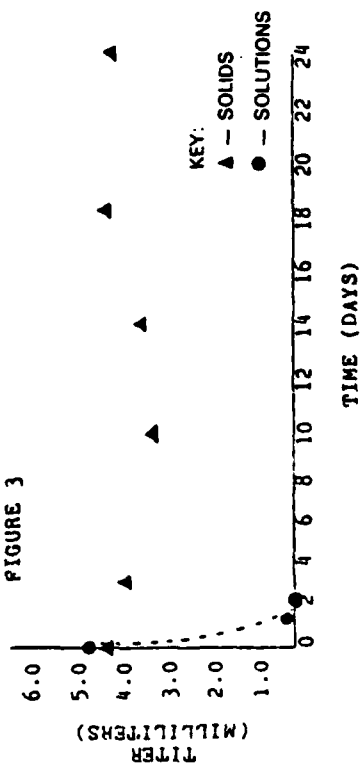
TABLE 4: PHYSICAL STATE OF OXIDIZER

Oxidizer	Physical State		Standing Time before Titration (min)
	as solid	in solution	
Lithium hypochlorite	dissolves slowly	slight sediment formation	0
Calcium hypochlorite	yields a chalky suspension, dissolves slowly	yields chalky suspension/sediment	0
PACE	dissolves quickly	yellowish precipitate forms	0
Sodium perborate	dissolves well	forms long crystalline needles when heated	25
Sodium peroxydisulfate	dissolves well	remained clear	50
Sodium percarbonate	dissolves well	yields precipitation/sediment	5
H-48	dissolves well; changed from white to tan with time	hot stored solution changes from clear to brown when heated	0- as solid 10- in solution

LITHIUM HYPOCHLORITE
FIGURE 1



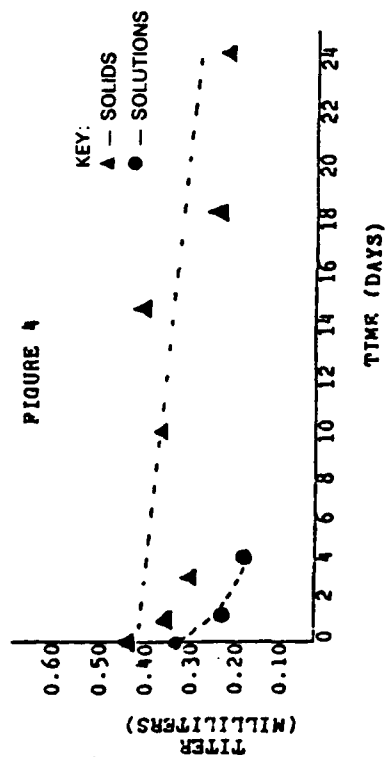
PACE
FIGURE 3



OXIDIZER STABILITY DATA
(for chlorine-based oxidizers)

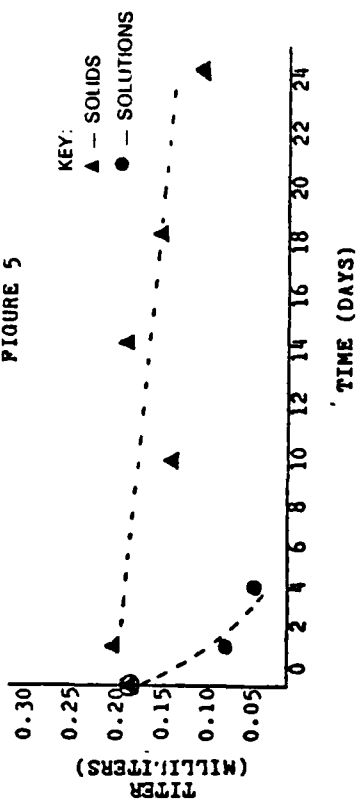
SODIUM PERBORATE

FIGURE 4



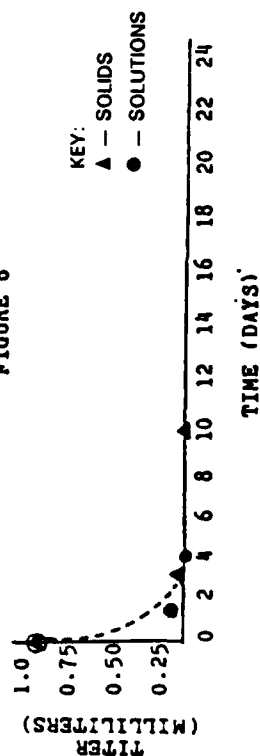
SODIUM PEROXYDISULFATE

FIGURE 5

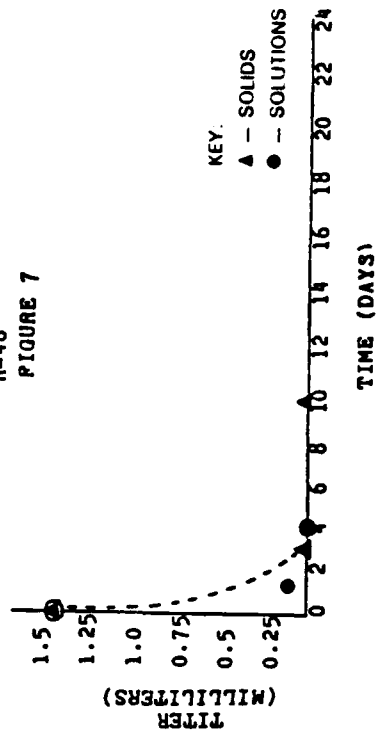


SODIUM PERCARBONATE

FIGURE 6



H-48
FIGURE 7



OXIDIZER STABILITY DATA
 (for oxygen-based oxidizers)

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